

ANALYSES OF CARBONATE ROCKS IN THE VIRGINIA PORTION OF THE MIDDLESBORO 1:100,000 SHEET

William W. Whitlock

INTRODUCTION

Virginia has large reserves of carbonate rocks in the Valley and Ridge province. More than 24,800,000 short tons of carbonate rocks (limestone and dolostone) were produced in Virginia in 1998, at a value of approximately \$173,600,000. These rocks are mined for a variety of uses including: steel and paper manufacture, water and sewage treatment, abatement of SO and NO emissions from coal-fired plants, mine safety dust, neutralization of acid mine drainage, cement, agricultural lime, and fillers and extenders.

In 1981, the Virginia Division of Mineral Resources (VDMR) initiated a sampling project to characterize the chemistry and reflectance of the carbonate rocks. Initial sampling began in the northern part of the Valley and Ridge province of Virginia. The results of the analyses were published in VDMR Publication 108 (Giannini, 1991) and Publication 135 (Giannini and Hostettler, 1994). Sampling began in southwest Virginia in 1984. Work has recently been completed in the area of the Middlesboro 1:100,000 sheet (Figure 1), where 422 limestone and dolostone samples were collected. Virginia's carbonate database, which includes samples from these areas, plus additional samples from other areas of Virginia, is available from William Whitlock at the Division of Mineral Resources in Abingdon (540/676-5829) or from Karen Hostettler at the Division of Mineral Resources in Charlottesville (804/951-6352).

The Middlesboro 1:100,000 sheet extends west of 83° in Virginia, including western Lee County in the Valley and Ridge physiographic province. Sampling was conducted in the Virginia portion of 12-7.5-minute quadrangles (Figure 2).

SAMPLING

In the area covered by the Middlesboro 1:100,000 sheet, 422 carbonate rock samples were collected. One or more samples were taken from each carbonate-bearing geologic formation, throughout the area, to provide a chemical characterization of the rocks. Chip samples as much as three inches in diameter were taken stratigraphically across rock outcrops at one to five feet intervals; depending on the extent of the outcrop and the heterogeneity or

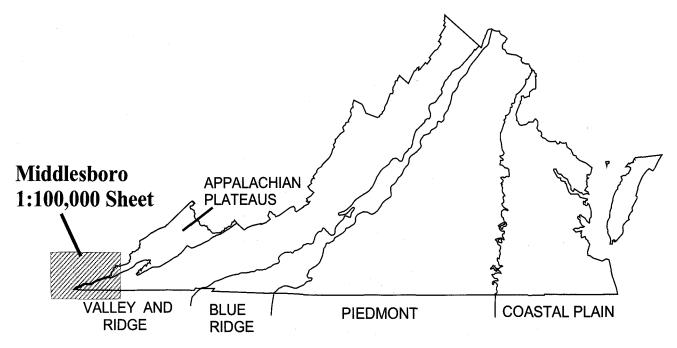


Figure 1. Index map of the study area, Middlesboro 1:100,000 sheet.

homogeneity of the rock. Formations were sampled at approximately one-mile intervals along strike. Across strike, samples were taken in each strike belt as well as on opposite sides of folds or faults. Impurities such as chert or shale were not sampled; however, they are noted in the column, <u>Rock Type</u>, in the database.

TESTING PROCEDURES

Knowledge of the chemical make-up is essential to determine potential uses of carbonate rocks. The rocks were analyzed for ten-part chemical composition, reflectance, trace elements, and chlorine composition.

Ten-part chemical analysis was conducted on each of the 422 samples. Each sample was crushed and ground to pass through 200-mesh and a portion through 325-mesh. Splits of the 200-mesh sample were then analyzed using X-ray fluorescence spectrometry for 10 basic compounds and element: CaCO; MgCO; SiO; Fe O; Al O; K O; Na O; TiO; P O; and S. Some samples were also analyzed for Cr O and MnO.

Reflectance analysis was conducted on selected samples. Each of the 325-mesh samples was compared visually to a sample of the same mesh size, which is known to have a brightness of 70 percent. A minimum of 70 percent brightness was used because this is generally the minimum value allowed by industry. Samples that appeared to have the same or greater brightness were then tested using a reflectance spectrophotometer. Values for amber, blue, and green were measured, then values for Yellowness, Brightness, and Whiteness were calculated.

Selected samples were analyzed for trace elements and chlorine content. These samples were selected to give a "cross-strike" representative sampling of the formations within the area.

Trace element analyses was conducted to identify 32 elements that might be contained in the rock. The elements might be deleterious for some uses. They may also indicate mineral deposits associated with the rock.

Chlorine content is especially important to determine in rocks that might be used in cement or concrete. It has been shown that when the total content of a raw cement mix exceeds 0.1 percent by weight of chlorine it may cause buildups within the preheater. It also may cause corrosion of steel used in reinforced concrete (Giannini and Hostettler, 1994).

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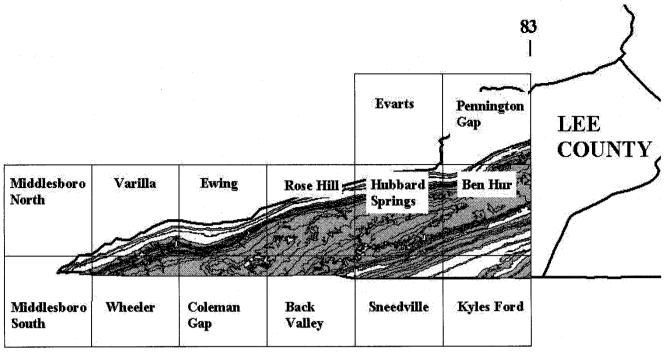


Figure 2. Map of carbonate rocks (gray stippled pattern) sampled in the 12 - 7.5-minute quadrangles in Virginia.

CHEMICAL USES

High-calcium limestone, high-purity dolostone, and the calcined (or burned) forms known as quicklime or hydrated lime have a variety of uses. Several of the main uses of chemical grade carbonate rocks are discussed below. These include: metallurgical and chemical processes of making steel, glass, and paper; as fillers and extenders; water and sewage treatment; and in the control of sulfur emissions from stacks of coal-fired plants.

METALLURGICAL AND CHEMICAL PROCESSES

A variety of metallurgical and chemical processes use limestone, dolostone, and lime. These include the manufacture of steel, glass, and paper.

High-purity limestone, dolostone, and lime are used in the steel making process to flux (precipitate out) impurities such as phosphorus, silica, and sulfur (Boynton, 1980). Limestone used in this process must have 95 percent or greater calcium carbonate (CaCO₃) and dolostone must have a combined CaCO₃ + Magnesium Carbonate (MgCO₃) of 95 percent or greater. Impurities such as SiO₂ that inhibit the reaction process should be kept to a minimum (Whitlock and Giannini, 1992).

The use of high-purity limestone, dolostone, or lime in the glass making process is often dependent on the type of glass being produced. Boynton (1980, p. 104) notes that high-calcium limestone or lime is used most often in flat or window glass, while dolostone or dolomitic lime is preferred for glass containers. The high MgO resists etching by chemical solvents and acids and reduces heat shock. High-calcium limestone with 98 percent or greater CaCO or high-purity dolostone with a combined 98 percent or greater CaCO + Mg CO is generally required for glass making. In addition, 0.06 percent or less Fe O is essential.

Limestone, in the form of lime, is used in the chemical process of paper-making. One waste-product of paper making is sodium carbonate. Lime is combined with the sodium carbonate to produce sodium hydroxide, which can then be reused in the paper-making process. Another use for lime is to produce bleach. Chlorine gas is bubbled through milk-of-lime. The resultant product is used to bleach the paper (Boynton, 1980, p.396-397). The limestone used in the production of lime for paper manufacturing has a minimum requirement of 95 percent CaCO.

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FILLERS AND EXTENDERS

Limestone is the primary source of carbonate material for use as industrial fillers and extenders. The CaCO of limestone is more inert than calcium oxide (CaO) of lime. Finely ground limestone is used as a white pigment filler and extender in paint; used in plastics to increase impact strength, rigidity, and improve flexibility; and used in paper manufacturing as a paper coating and also as an integral filler to fill the voids in the paper. Limestone is also used as a filler in rubber. Limestone used in rubber has a more stringent chemical requirement of 98 percent or greater CaCO. Physical characteristics are of primary importance in the use of limestone for fillers and extenders. Industry standards generally requires a minimum reflectance value of 70 percent brightness. Strict size specifications restrict the forms of limestone that can be used as fillers and extenders. These forms include limestone pulverized to a 100-mesh size; intensely ground limestone, called whiting; or precipitated calcium carbonate. Precipitated calcium carbonate is a chemically derived, micro-fine lime product (Boynton, 1980, p.108-113).

WATER AND SEWAGE TREATMENT

Lime produced from high-calcium limestone is used in the treatment of water and sewage. Lime is used in water treatment to remove the temporary (bicarbonate) hardness, to purify the water against bacteria, to reduce coagulate suspended solids and reduce turbidity, and to reduce the acidity of water by raising the pH.

In sewage treatment lime is used to increase the pH. This results in the destruction of many pathogens, reduction in odor, improved sludge filtration and conditioning, and removal of phosphate by precipitation (Boynton, 1980, p.402-407).

Limestone used to produce the lime generally must have a CaCO of 95 percent or greater.

CONTROL OF SULFUR DIOXIDE EMISSIONS

Increased environmental concerns about the gases emitted from coal-fired plants has resulted in the need for limestone that can be used to removed sulfur before it is released from the stacks. Limestone and lime are used in two methods to reduce the sulfur.

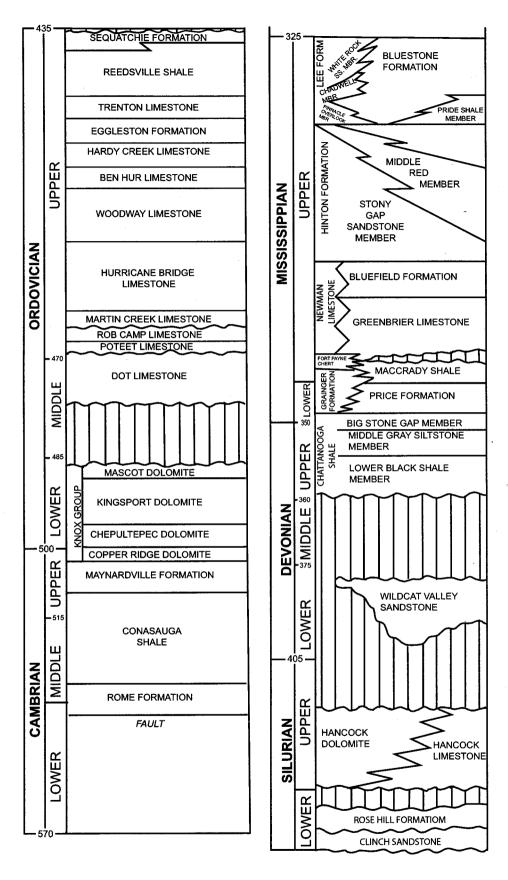
In the fluidized bed combustion method, coal and limestone are introduced into an air distribution grid at the firing zone. Air is forced into the grid creating a suspended bed of material. As combustion occurs, the limestone is converted to CaO, which then reacts with the SO, to form CaSO (gypsum) precipitate, which removes the SO from the gases.

In the flue gas desulfurization, or scrubber method, ground limestone or lime is sprayed into the gas that results from combustion of coal. This is above the firing zone, but before the gas is released from the stack. The resultant reaction causes the lime or limestone to react with the SO, which results in precipitation of CaSO. Limestone used in this process requires CaCO of 90 percent or greater and MgCO of 5 percent or less.

GEOLOGY AND CHEMISTRY OF SELECTED CARBONATE ROCKS

Carbonate rocks in the area of the Middlesboro 1:100,000 sheet of the Valley and Ridge province are mainly Cambrian to Ordovician in age, with lesser amounts of Silurian to Missisippian age (Figure 3). These rocks range in chemical composition from the Upper Ordovician age Rob Camp Limestone that averages more than 96 percent CaCO for 11 samples to the Cambrian age Copper Ridge Dolomite that averages more than 42 percent Mg CO for 25 samples.

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Geologic Time in m.y.

Figure 3. Stratigraphy of the Valley and Ridge province in the Middlesboro 1:100,000 sheet (modified from Rader, 1982).

The Rob Camp Limestone, named by Miller and Brosgé (1950), is equivalent to the Mosheim Limestone of Miller and Fuller (1954). In this area it is primarily micrograined, very thick-bedded limestone that ranges in thickness from a thin layer up to 153 feet (Miller and Fuller, 1954, p. 76; Miller and Brosgé, 1954, p.41). The Rob Camp Limestone was sampled at 11 locations throughout the area. Average chemical values in these samples of the formation were 96.64 percent CaCO, 1.9 percent MgCO, 1.31 percent SiO, and 0.09 percent Fe O. Brightness of the formation averaged 80.22 percent. With these values, if the required thickness can be located, this formation has the potential for use in: water and sewage treatment, chemical use in the paper industry and in metallurgical processes, in fillers and extenders for paper and paint and possibly rubber-making processes, and in sulfur emissions control.

The Copper Ridge Dolomite in the Middlesboro 1:100,000 sheet is composed of two informal members. The lower member is dark-gray to dark-brown, medium- to coarse-grained, dolostone in very thick beds. The dark-colored dolostone commonly emits a petroliferous odor when broken. The upper member is light-gray, fine- to coarse-grained dolostone. Chalcedonic and oolitic chert is common but most abundant near the top of the formation. The formation is 800 to 850 feet thick (Miller and Fuller, 1954, p. 42-45; Miller and Brosgé, 1954, p.18-20). Twenty five samples were collected from the Copper Ridge Dolomite (Table 1). Average chemical composition for the 25 samples taken are 53.35 percent CaCO, 42.64 percent MgCO, 2.98 percent SiO, and 0.25 percent Fe O. Average brightness is 78.08 percent. Even though the Copper Ridge in this area averages approximately 95 percent combined CaCO and MgCO the high SiO level average of 2.98 percent, probably due to the chert found in the formation, restricts its chemical use to fillers and extenders.

Table 1. Average of analyses for the Rob Camp Limestone and Copper Ridge Dolomite sampled in the Middlesboro 1:100,000 sheet.

FORMATION	# of Samples Collected	Min. CaCO %	Max. CaCO %	Min. MgCO 3%	Max.MgCO %	Min. SiO ₂ %	Max. SiO %	Mini. Fe O %	Max.Fe O %	Minimum Brightness %	Maximum Brightness %	Minimum Interval (feet)	Maximum Interval (feet)
Rob Camp	11	94.49	98.16	1.26	3.08	0.66	2.91	-0.01	0.22	77.70	82.85	1.00	51.00
Copper Ridge	25	49.88	55.86	38.57	44.76	1.24	9.96	-0.01	0.48	71.50	85.55	3.00	64.00

Chemistry of the carbonate-bearing formations have a wide range throughout the area. In reviewing the database there are a number of formations which have average CaCO and/or MgCO content close to the required levels to make them economically useful as chemical grade limestone or dolostone. Review of individual samples may identify formations that have economic potential in specific localities.

The Ordovician age Hurricane Bridge and Woodway limestones are exposed throughout the area of the Middlesboro 1:100,000 sheet. The Hurricane Bridge Limestone is equivalent to the lower part of the Lowville Limestone as described by Miller and Fuller (1954). The formation is 288 to 368 feet of tan and gray, micrograined, thin-bedded limestone with zones of micrograined, thick-bedded limestone (Miller and Fuller, 1954, plate 9; Miller and Brosgé, 1954, plate 3). The Woodway Limestone is equivalent to the upper part of the Lowville Limestone as described by Miller and Fuller (1954). It is 244 to 288 feet of tan and gray, micrograined to medium-grained limestone in thin, even beds (Miller and Fuller, 1954, plate 9; Miller and Brosgé, 1954, plate 3). Along strike to the southwest in Tennessee, the Hurricane Bridge Limestone is described as 260 to 300 feet thick and is divisible into an upper gray to pink, fossil-fragmental limestone, and a lower gray, very fine to fine-grained, cherty limestone (Brent, 1987). Brent (1987) also described the Woodway Limestone as 200 to 250 feet of fossil-fragmental, very-fine- to fine-grained, nodular limestone with chert zones near the base and top.

Thirty eight samples of the Hurricane Bridge Limestone collected throughout the Middlesboro 1:100,000 sheet

Table 2. Analytical results for samples of Woodway and Hurricane Bridge limestones sampled in the northeastern Sneedville 7.5 -minute Quadrangle.

Sample Number	Quadrangle	Formation	Rock Type	Interval (feet)	CaCO %	Mg CO %	SiO %	Fe O %	Whiteness %	Brightness %
030C-012	Sneedville	Woodway	Limestone,	47.00	92.63	2.89	2.61	0.34	79.69	79.18
030C-013	Sneedville	Hurricane Bridge	Limestone	72.00	94.77	1.42	2.05	0.39	81.36	80.96
030C-014	Sneedville	Hurricane Bridge	Limestone	40.00	95.84	1.40	1.77	0.38	80.19	79.71

averaged 91.79 percent CaCO, which excludes it from many chemical grade uses. Twenty-five samples of Woodway Limestone were also collected in the area of the Middlesboro 1:100,000 sheet. The CaCO in these samples averaged 93.25 percent. However, the Hurricane Bridge and Woodway limestones have greater economic potential in one locality in the northeastern part of the Sneedville 7.5-minute quadrangle, along State Road 612, approximately 3700 feet east of the junction of State Roads 665 and 612. At that locality two samples of a 112 feet interval of the Hurricane Bridge Limestone had 95.84 percent and 94.77 percent CaCO. Immediately above the Hurricane Bridge Limestone, a sample of 47 feet of Woodway Limestone contained 92.63 percent CaCO. These formations, in particular the Hurricane Bridge Limestone, have potential for use in chemical and metallurgical processes, fillers and extenders, water and sewage treatment, and the control of SiO emissions of coal-fired plants.

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COALFIELD MAPS-ON-DEMAND AVAILABLE

The following Maps-On-Demand for the mined portion and coalbed extent for the Southwest Virginia Coalfield are now available. The price for each copy is \$18.00 plus 4.5% sales tax for maps mailed to Virginia addresses.

MOD-1 Mined portion and extent of Pocahontas No. 3 coalbed in Southwest Virginia, by D. B. Spears, J. E. Nolde, and R. S. Sites, 1997, scale 1:100.000.

MOD-6 Mined portion and extent of the Phillips (Fireclay/Hazard #4) coalbed in Southwest Virginia, by R. S. Sites, D. B. Spears, and R. S. Hope, 1998, scale 1:50,000.

MOD-7 Mined portion and extent of the Imboden (Pond Creek/Lower Elkhorn) coalbed in Southwest Virginia, by R. S. Sites, D. B. Spears, and R. S. Hope, 1998, scale 1:100,000.

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- MOD-8 Natural gas field in the Virginia portion of the Appalachian basin, by J. E. Nolde and D. B. Spears, 1999, scale 1:100,000.
- Mined portion and extent of the Taggart (Darby/upper coal in Elkhorn #3 zone) coalbed in Southwest Virginia, by Roy S. Sites, MOD-9 Rebecca S. Hope, and David B. Spears, 1999, scale 1:50,000.
- Mined portion and extent of the Taggart Marker (Kellioka/lower coal in Upper Elkhorn #3 zone) coalbed in Southwest Virginia, by Roy S. Sites, Rebecca S. Hope, and David B. Spears, 1999, scale 1:50,000.

 Mined portion and extent of the Wilson (Collier/ Upper Elkhorn #2/ a coal in Harlen/Alma zone) coalbed in Southwest Virginia, by MOD-10
- MOD-11 Roy S. Sites, Rebecca S. Hope, and David B. Spears, 1999, scale 1:100,000.
- MOD-12 Mined portfion and extent of the Kelly (upper coal in Lower Elkhorn zone (Pond Creek Rider?)) coalbed in Southwest Virginia, by Roy S. Sites, Rebecca S. Hope, and David B. Spears, 1999, scale 1:100,000.
- Mined portion and extent of the Lower Horsepen coalbed in Southwest Virginia, by Roy S. Sites, Rebecca S. Hope, and Jack E. MOD-13 Nolde, 1999, scale 1:150,000.
- Mined portion and extent of the Morris (No. 11 / Hazard No. 5A) coalbed in Southwest Virginia, by Roy S. Sites, Rebecca S. Hope, MOD-14 and David B. Spears, 1998, scale 1:50,000.
- MOD-15 Mined portion and extent of the High Splint (No. 12) coalbed in Southwest Virginia, by Roy S. Sites, Rebecca S. Hope, and David B. Spears, 1998, scale 1:50,000.
- MOD-16 Mined portion and extent of the Pardee (No. 10 / upper coal of the Hamlin coal zone) coalbed in Southwest Virginia, by Roy S. Sites, Rebecca S. Hope, and David B. Spears, 1998, scale 1:50,000.
- Mined portion and extent of the Low Splint (No. 6 / a coal in Creech & Amburgy coal zone) coalbed in Southwest Virginia, by Roy MOD-17 S. Sites, Rebecca S. Hope, and David B. Spears, 1998, scale 1:150,000.
- MOD-18 Mined portion and extent of the War Creek (Beckley) coalbed in Southwest Virginia, by Roy S. Sites, Rebecca S. Hope, and Jack E. Nolde, 1999, scale 1:150,000.
- MOD-19 Mined portion and extent of the Fire Creek coalbed in Southwest Virginia, by Roy S. Sites, Rebecca S. Hope, and Jack E. Nolde, 1999, scale 1:150,000.
- Mined portion and extent of the Addington (uppermost Clintwood Marker?) coalbed in Southwest Virginia, by Roy S. Sites and MOD-20 Rebecca S. Hope, 2000, scale 1:100,000
- Mined portion and extent of the Lyons (Eagle of Virginia) coalbed in Southwest Virginia, by Roy S. Sites and Rebecca S. Hope, 2000, MOD-21 scale 1:100,000.
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- Mined portion and extent of the Jawbone coalbed in Southwest Virginia, by Roy S. Sites and Rebecca S. Hope, 2000, scale
- MOD-34 Mined portion and extent of the Splashdam coalbed in Southwest Virginia, by Roy S. Sites and Rebecca S. Hope, 2000, scale 1:100,000.